

# PATENT SPECIFICATION

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## (54) PROCESS FOR RECOVERY OF CLEAN POLYESTER MATERIALS

(71) We, HORIZONS RESEARCH INCORPORATED, a corporation organised and existing under the laws of the State of Ohio, United States of America, of 23800 Mercantile Road, Cleveland, Ohio 44122, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for recovering clean polyalkylene terephthalate polyester (hereinafter referred to as "polyester") and other materials from photographic film and magnetic recording tape comprising such polyester, which is preferably, but not exclusively, polyethylene terephthalate. The polyester is recovered as one product and the other materials which are non-polyester materials are recovered separately.

The present invention is particularly concerned with the recovery of clean polyester and silver values from polyester photographic film, but it will be readily apparent that the process is applicable to other raw materials such as magnetic recording tapes from which the polyester and magnetic iron oxide can be recovered separately and to still other raw materials.

Polyester film is being used in increasing amounts for photographic support, magnetic recording tape, graphic arts materials, electrical insulation, and other applications requiring a clear, strong, dimensionally stable chemically resistant film. In some of these applications, as in photographic film, the polyester is coated with binders, adhesives, and metal compounds. Because of the non-polyestered materials associated with the polyester, used polyester photographic film has little value other than the intrinsic value of the silver contained in the coating. One current practice for recovering silver from used photographic film utilizing a polyester support is to incinerate the film and reclaim silver from the ash by pyrometallurgical processing.

The economics of this process are not favourable at present silver prices.

Other methods which have been proposed for recovering photographic support material are described, for example, in the Specifications of United States Patent No. 3,047,435, Canadian Patent No. 626,996, and British Patent No. 1,134,967. These methods have used aqueous solutions of alkali, surfactant or enzymes as well as non-aqueous alkaline glycols to remove the emulsion or other coating layers. These previous methods are limited in practice in that the aqueous solutions of alkali, surfactants, or enzymes employed therein will not remove polymeric subcoatings associated with polyester films without seriously degrading the polyester, while nonaqueous alkaline glycols will not remove all waxes and oils from the film surface and rapidly become saturated with gelatin. Therefore they are not suitable for recovering both polyester and coating layers from used photographic film.

It would be desirable to convert used polyester films into clean polyester which can be used as a raw material for the production of fibres or film, or other articles. It would also be desirable to recover the photographic material coated on the polyester base, which material can be further processed to recover silver. Recovery of the polyester which resists biodegradation and of the silver in forms which can be reused will reduce solid waste disposal problems as well as reduce depletion of natural resources by permitting recycling these materials.

According to the present invention there is provided a process for the separate recovery of clean polyalkylene terephthalate polyester and contaminants associated therewith from photographic film or magnetic recording tape comprising such polyester, which process comprises:

- (1) wetting the polyester material at a temperature of from 100°C to 180°C for a time sufficient to remove the contaminants from the polyester material with an

- alkaline aqueous solution of an organic liquid;
- (2) separating the polyester material from the solution and contaminants; and
- 5 (3) recovering the resulting clean polyester material.

The alkaline aqueous solution may comprise an alkylene glycol, such as ethylene glycol or propylene glycol, containing 0.1% to 5% by weight of an alkali metal hydroxide, preferably sodium hydroxide, and 2% to 15% by weight of water. Alternatively, the organic liquid may be mono- or di-ethanolamine. The temperature at which the wetting is effected is preferably from 140°C to 160°C.

With the present process it is possible to produce two useful products from polyester photographic film, namely: (1) clean polyester materials suitable for reuse in the manufacture of extruded film or fibre, unextruded fibres, or for making shaped articles, and

20 (2) separated coating sludge which contains the silver and other constituents in the photographic layer on the polyester base.

The present process may be conducted as a single treatment which separates the polyester, preferably polyethylene terephthalate, film base from the photographic emulsion, the subcoat usually present to improve adhesion of the silver-containing layer to the film base, and other dirt and oils associated with used film.

It is also possible to carry out the present process with recycle of reagents in a closed system, thereby eliminating pollution to the environment from contaminating vapours or liquid effluents.

As indicated above, the present process is particularly suited to the removal of coatings and subcoatings from polyester photographic film. In such films, the film base is usually polyethylene terephthalate and the coatings on such base comprise a variety of minerals, binders, adhesives, waxes, oils, or other materials placed on the film during manufacture or subsequent use. The subcoating may consist of a copolymer of vinyl chloride or vinylidene chloride together with an acid such as itaconic, acrylic or methacrylic acid, the subcoating serving to promote adhesion of the usual gelatin-cellulose acetate composition photographic coatings to the polyester film base.

In order to recover clean polyester and a sludge containing the coating materials, a preferred embodiment of the present process comprises the steps of:

- (1) wetting the polyester photographic film with an aqueous alkaline solution of an organic solvent which will loosen and detach both the coating and subcoating from the surface of the polyester film base, emulsify oils and waxes, and dis-
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solve binders associated with the coating constituents;

- (2) separating the polyester film from the reagent and removed coating and subcoating;

- (3) separating the removed coating materials from the reagent, to produce a sludge containing a metallic silver and a clarified reagent;

- (4) rinsing the separated film with the clarified reagent; and

- (5) recycling the clarified reagent from the rinse stage (4) to step (1) in carrying the process forward on additional photographic film.

In order to enable the invention to be more readily understood, reference will now be made to the accompanying drawings, which illustrate diagrammatically and by way of example two embodiments thereof, and in which:—

Figure 1 is a flow sheet of one embodiment of the process of the present invention, and

Figure 2 is a flow sheet of a modification of the process illustrated in Figure 1.

The flow sheet shown in Figure 1 schematically depicts a preferred embodiment of the present process. In this embodiment the developed or undeveloped photographic film 10, entering the process as sheet or roll, or individual pieces of irregular size and shape, is chopped or cut in a granulator 12 to a flake of approximately 1/4 inch diameter. The flake is then charged into a closed heated vessel or contactor 14 in which it is brought into physical contact with ethylene glycol containing from 0.1% to 5% sodium hydroxide and 2% to 15% water, by weight. The vessel and its contents are heated to a temperature of from 100°C to 170°C, preferably from 140°C to 160°C, and the mixture of flake and glycol solution is agitated for a time sufficient to loosen the coating materials from the polyester surface, agitation from 5 to 15 minutes being usually sufficient to accomplish the desired separation.

After the separation is complete and all of the coating has been stripped from the flake, the film-glycol slurry is pumped to a coarse separator 16 containing a sieve of sufficient size, about 0.30 inch opening, to retain the film while allowing the ethylene glycol solution slurry containing the coating materials to pass to a separator tank or collector 20. The separator 20 can be a simple closed tank containing a mesh collecting basket or a continuous belt filter, as the process is not dependent upon the type of equipment used for the separation.

The effluent 22 from the separation stage 20 is pumped to a centrifuge 24 for removal of the suspended coating materials from the ethylene glycol solution. Other types of pro-

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cessing equipment, for example, pressure or vacuum filters, may be used for this step provided that such alternative equipment is able to clarify the ethylene glycol solution to a maximum of 0.05% suspended solids by weight; a necessary requirement since the clarified liquid 28 is fed to a rinse vessel 29 where it is used to rinse the stripped film of any coating residue that may have remained after the coarse separation in separator 16. The ethylene glycol solution is then recycled by a conduit 30 to the closed heated vessel 14. The clean, rinsed polyester is recovered as a product 32.

The solids, discharged from the centrifuge 24 as a thickened sludge 26 contain silver. Further recovery of the contained silver and other by-products can be effected by any of a variety of procedures.

The polyester flake 32 is, after rinsing with the clarified centrifuge effluent 28, clean and suitable as a raw material for making extruded film or fibre or other shaped articles.

A distinct advantage of this process is the ability to operate in closed vessels and to recycle the glycol solution through the rinse to the starting reactor, thereby minimizing reagent loss to the atmosphere and eliminating the need for additional rinse solutions.

Feed of smaller or larger particle size than 1/4 inch may be used in the process. For example, a particle size as small as 0.030 inch can be treated if the sieve opening in the coarse separator 16 is chosen so as to retain a 0.030 inch particle. The equipment can be modified to accommodate large sheets, 1 to 2 feet across or larger, by increasing the size of the vessels, piping and other equipment proportionally.

Instead of ethylene glycol other reagents such as alkaline propylene glycols, mono-ethanolamine, and di-ethanolamine, have been used in the process with equal success. Reagents other than those named would also give acceptable results providing that such other reagents are miscible with water and are alkaline or are made alkaline as determined by titration with a mineral acid such as hydrochloric acid within the limited of 0.01 N to 5 N calculated as equivalent sodium hydroxide.

The process can be modified to produce clear polyester film in continuous strip form as schematically shown in Figure 2. Developed or undeveloped film entering the process as a roll 100 is fed by driven rollers 102 and 104. The continuous strip 100 passes through a pool 106 of heated ethylene glycol solution containing 0.1% to 5% sodium hydroxide and 2% to 15% water, by weight, at a temperature of from 100°C to 170°C, preferably from 140°C to 160°C, in a heated contactor 114, the speed of the strip being adjusted so that the residence time of the

strip 100 in the pool of ethylene glycol will be sufficient to loosen the coating materials from the polyester surface. The residence time can be increased by slowing the rate of the strip travel. Loosening of the coating is increased by flexing the strip, e.g. by passing it around a number of rollers immersed in the pool of ethylene glycol solution.

The strip leaves the reactor 114 and passes to an adjacent rinse vessel 129. The effluent 115 from the contact 114 is pumped to a centrifuge 124 or other separating device as described in the process of Figure 1, and the resulting clarified solution 128 is used to rinse the strip after which the solution is pumped back to the heated vessel 114.

The coating solids can be handled as previously stated. The clean polyester 132 in continuous strip is suitable as a raw material for un-extruded fibres or other strip applications and the coating sludge 126 is processed to recover the silver and other values as noted above.

The invention will now be further illustrated by the following non-limiting Examples.

#### Example 1

Twenty pounds of aerial photographic film having a polyethylene terephthalate base were granulated to a 1/4 inch nominal particle size and placed in a heated vessel containing 100 gallons of ethylene glycol with 1% by weight sodium hydroxide and 10 gallons of water at 150°C and slowly mixed. After a short time (about 1 minute), the coating was seen to be lifting from the surface of the film base. Stirring continued for 15 minutes to ensure complete contact of liquid with all pieces of film.

After the 15 minute residence time in the heated vessel, the mixture was pumped to a strainer containing a screen of 0.030 inch opening which allowed the ethylene glycol solution containing the solid coating materials to pass, but which retained the film base flake. The effluent was then pumped through a pressure leaf filter which retained the coating materials. The clarified ethylene glycol solution was again pumped to the strainer to rinse any remaining coating particles from the film base particles, then recycled to a storage tank for use with another batch of film.

The cleaned film was suitable as a raw material for extrusion as a film or compounding to a moulding composition. The coating sludge remaining on the filter was processed to recover the silver by pyrometallurgical techniques.

#### Example 2

Ten sheets of 14 inch×17 inch X-ray photographic film having a polyethylene terephthalate base and weighing about 1 lb, were

- placed in a steel tank containing 15 gallons of ethylene glycol with 0.5% by weight sodium hydroxide and 0.5 gallons of water at 180°C. The mixture was stirred slowly. After 2 minutes the coating containing the silver was seen to be lifting from the film and emulsifying in the alkaline ethylene glycol. Stirring was stopped after 10 minutes and the mixture was then poured through a sieve with 0.30 inch openings. The sieve effluent was filtered through a Buchner vacuum filter and the clarified effluent poured over the polyester sheets to flush off any residue of coating from the film base. The cleaned sheets were suitable as raw material for extrusion, fibrilating or compounding. The coating sludge was removed from the filter and processed to recover the silver by pyrometallurgical techniques.

#### Example 3

- A roll of 9-1/2 inch wide aerial film having a polyethylene terephthalate base was cleaned on a modified continuous photographic film processing machine. As modified the film was fed to drive rolls and directed by means of idler and take-up rolls through two tanks.

The first tank contained 25 gallons monoethanolamine and 2 gallons of water at 140°C. The second contained ten spray nozzles which

directed a spray of filtered monoethanolamine solution at the film strip. The film was run at about 2 linear feet per minute which gave a film residence time of 12 minutes in the first monoethanolamine solution tank and an equal time in the monoethanolamine solution in the rinse tank. Liquid and solids therein discharged from the bottom of the first tank were passed through a pressure leaf filter to remove suspended particles of coating material, and the clarified reagent was sprayed onto the moving film strip in the second tank. Overflow from the rinse was recycled to the first treating tank.

The cleaned strip film was suitable as raw material for extrusion, fibrilating or compounding or it could be used, as recovered, in the same manner as virgin polyester film, for strapping tape, electrical insulation, and other known applications. The sludge removed from the filter was processed by pyrometallurgical techniques into metallic silver.

#### Examples 4—15

Aerial photographic film having a polyethylene terephthalate base was chopped to about 1/4 inch particle size and 100 gm. of the flakes were placed in each of a series of 2 litre beakers containing 1 litre of reagent as shown in the following Table:

Example	Wt. % Sodium Hydroxide In Glycol	Wt. %, Water in Glycol	Temperature (°C.)	Results
4	0.00	0.0	150	Unsatisfactory
5	0.10	5.0	90	Unsatisfactory
6	0.10	10.0	100	Satisfactory
7	0.10	15.0	150	Satisfactory
8	0.10	2.0	170	Satisfactory
9	0.10	5.0	175	Satisfactory
10	1.00	5.0	90	Unsatisfactory
11	5.00	0.0	90	Unsatisfactory
12	5.00	15.0	150	Satisfactory
13	5.00	10.0	170	Satisfactory
14	5.00	5.0	175	Satisfactory
15	5.00	0.0	170	Unsatisfactory

- It is to be noted that the use of ethylene glycol to remove the subbing layer from a polyester film base is described in the Specification of British Patent No. 1,134,967, but the present invention treats used film for removal of both the subcoat and the silver containing overcoating and other surface contaminants in a single treatment, as compared with the procedure in the British Patent which involves a preliminary step for removing the emulsion layer and does not remove all surface contaminants present on used film.

#### WHAT WE CLAIM IS:—

1. A process for the separate recovery of clean polyalkylene terephthalate polyester and contaminants associated therewith from photographic film of magnetic recording tape com-

prising such polyester, which process comprises:

- (1) wetting the polyester material at a temperature of from 100°C. to 180°C. for a time sufficient to remove the contaminants from the polyester material with an alkaline aqueous solution of an organic liquid;
- (2) separating the polyester material from the solution and contaminants; and
- (3) recovering the resulting clean polyester material.

2. A process as claimed in Claim 1, wherein the polyester material is a photographic film consisting of a polyester base, a co-

polymer subcoating on said base and a photo-sensitive emulsion on said subcoating.

3. A process as claimed in Claim 1 or 2, wherein the temperature is from 140°C. to 160°C.

4. A process as in any preceding Claim, wherein the alkaline aqueous solution containing removed contaminants is separated into a clarified liquid and a sludge which contains the contaminants, and wherein the clarified liquid is used to rinse the clean polyester base.

5. A process as claimed in Claim 4, wherein the clarified liquid is recycled from the rinse step to the step of contacting the polyester material.

6. A process as claimed in any preceding Claim, wherein said solution comprises an alkylene glycol containing 0.1% to 5% by weight of an alkali metal hydroxide and 2% to 15% by weight of water.

7. A process as claimed in Claim 6, wherein the alkylene glycol is ethylene glycol and the alkali metal hydroxide is sodium hydroxide.

8. A process as claimed in Claim 7, wherein the glycol is propylene glycol.

9. A process as claimed in any of Claims 1 to 5, wherein the organic liquid is mono- or di-ethanolamine.

10. A process as claimed in any preceding Claim, wherein the polyester is polyethylene terephthalate.

11. A process for the separate recovery of clean polyalkylene terephthalate polyester and contaminants associated therewith from photographic film or magnetic recording tape comprising such polyester substantially as hereinbefore described with reference to Figure 1 or Figure 2 of the accompanying drawings, or in any one of Examples 1 to 3, 6 to 8, and 12 to 14 of the foregoing Examples.

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**FIG. 1.**

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graph TD
    10[Polyester Photographic Film] --> 12[Granulator]
    12 --> 14[Contactor]
    14 -- 15 --> 16[Coarse Separator]
    16 --> 20[Slurry]
    16 -- "Stripped Polyester" --> 28[Centrifuge]
    20 -- 22 --> 24[Centrifuge]
    24 -- "Coating Solids" --> 26[Coating Sludge]
    24 -- "Clarified Liquid" --> 28
    28 --> 32[Clean Polyester]
    28 -- 29 --> 30[ ]
    30 -- 30 --> 14
    30 --> 32
    32 --> M[To Molding Machine]
    26 --> R[To Silver Recovery]
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The flowchart illustrates the process for recovering silver from polyester photographic film. The process begins with Polyester Photographic Film (10), which is fed into a Granulator (12). The output of the Granulator (12) is sent to a Contactor (14). From the Contactor (14), the material (15) is sent to a Coarse Separator (16). The Coarse Separator (16) produces two streams: a Slurry (20) and Stripped Polyester, which is sent to a Centrifuge (28). The Slurry (20) is sent to the Centrifuge (24). The Centrifuge (24) produces two streams: Coating Solids (26) and Clarified Liquid (28). The Coating Solids (26) are sent to Coating Sludge (26), which is then sent to Silver Recovery. The Clarified Liquid (28) is sent to the Centrifuge (28). The Centrifuge (28) produces two streams: Clean Polyester (32) and a stream (29) that is sent to a junction (30). The junction (30) also receives Treating Liquids and sends a stream (30) back to the Contactor (14). The Clean Polyester (32) is sent to the Molding Machine.

The diagram illustrates a silver recovery process. A feed stream 100 enters a Contactor 106 through a valve 102 and a filter 104. The Contactor 106 contains a liquid 114 and a stirrer 108. The output of the Contactor 106 goes to a Centrifuge 124 through a line 115. The Centrifuge 124 separates the liquid from the solid. The liquid 128 goes to a Rinse tank 129, which then feeds back into the Contactor 106. The solid 126 goes to a Coating Sludge unit, which then feeds into a To Silver Recovery Unit.